

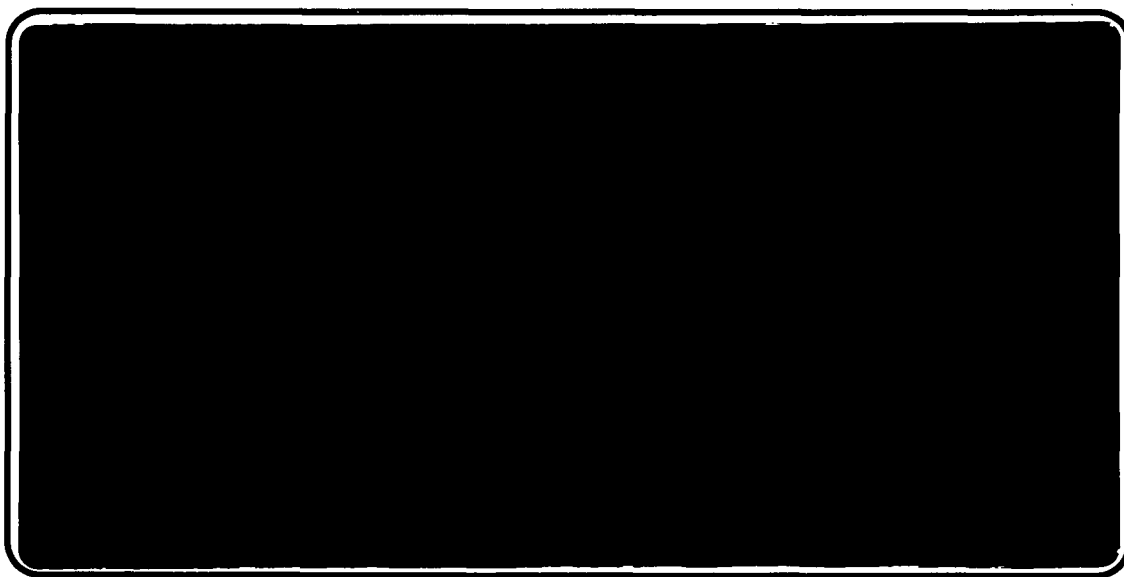


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**IN SEARCH OF THE IDEAL PULP MILL**

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## IN SEARCH OF THE IDEAL PULP MILL

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Raleigh, North Carolina - An international cadre of pulping and bleaching experts converged on the campus of North Carolina State University on March 18 to spend three days educating an audience of more than 200 delegates. The occasion was the 1991 Workshop on Emerging Pulping and Chlorine-Free Bleaching Technologies, staged by the university's Department of Wood and Paper Science, under the guidance of workshop chairman Josef S. Gratzl.

The large size of the audience, in a time of recession-induced travel restrictions, spoke to the high degree of importance currently attached by the industry to the topic. Market pressures from abroad, combined with growing concern over the domestic regulatory climate, provide strong incentives for pulp mills to position themselves at the forefront of technologies for reducing chlorine use. These include extended delignification in both batch and continuous processes; oxygen delignification and methods, such as pretreatments, to increase its ability to displace chlorine; bleaching with ozone; peroxide bleaching; and more unconventional methods that may have potential for limiting chlorine use. The last category includes enzymatic bleaching, use of peracids, solvent pulping and biopulping. All were covered in considerable detail by a slate of speakers known for their contributions in the areas discussed. In addition, and in keeping with the need for basic understanding that goes with the intelligent choice and application of any technology, several speakers reviewed relevant underlying principles. The meeting concluded with two panel discussions dealing with future directions and research and development needs. The program comprised a total of 27 presentations, including those of the panelists.

## BUILDING BRIDGES

In a characteristically eloquent keynote address, Dr. Alfred H. Nissan seized the opportunity to impress upon the audience the urgency of establishing strong links between universities and the industry. Among the issues he dealt with was the critical need for the industry to shed the smokestack image and to replace it with the "high-tech" designation it deserves. Industry must continue to be a "social climber on the ladder of technology," and this will require stronger industry-university linkages than we have yet achieved. In establishing linkages, the needs of both the university and the industry must be addressed. Among the needs of the former is increased enrollment in science and engineering programs; industry can help by communicating to very young students messages concerning the importance of science. One such message is that, in spite of such debacles as Hiroshima and the

hole in the ozone layer, only science and technology can correct many of modern society's problems, including those brought on by earlier misapplications of science. To interact with the universities in a truly beneficial way, industry must somehow be admitted to the circle of informal communication that exists at the leading edge of university research. Possible ways of doing this, according to Nissan, are encouraging industry as well as university scientists to contribute to the pool of basic science, granting sabbatical leaves to be spent working in the university environment and being receptive to university scientists who wish to work in the industrial milieu.

Following the keynote address, Tom McDonough of the Institute of Paper Science and Technology introduced the more technical part of the program. He presented an overview of the relevant technologies for minimizing the formation of chlorinated organic byproducts, viewing each as a method of decreasing the concentration of chlorine and/or organic precursor. Known effects on formation of AOX, dioxins, chlorophenols, and chloroform were reviewed, as well as effects on lignin removal and cellulose degradation. This was followed by presentations examining individual technologies in greater depth.

## DOING IT IN THE DIGESTER

Conceptually, the most attractive route to decreased chlorine use for lignin removal in the bleach plant is to arrange for the lignin to be removed in the digester instead. The degree to which this can be done was the subject of several presentations, beginning with a recapitulation of the general principles of alkaline delignification by Prof. Gratzl. Hasan Jameel of N.C. State then gave a spirited review of extended delignification in batch processes. He pointed out that, to achieve greater selectivity and allow cooking to lower kappa number, a process should ideally incorporate several features: low and uniform alkali concentration; high sulfide concentration, especially at the onset of bulk delignification; low dissolved lignin concentration at the end of the cook; and low temperature discharge of the chips from the digester. He concluded with a discussion of three commercial systems for batch extended cooking.

Extended delignification in continuous digesters (modified continuous cooking, MCC) was discussed by Nils Hartler of The Royal Institute of Technology in Stockholm. In addition to reviewing established MCC principles, Dr. Hartler discussed more recent developments, including extending the cook into the wash zone ("poor man's MCC"), adding polysulfide and/or AQ to overcome yield and beatability disadvantages of MCC pulps, and precooking with a sulfide-enriched liquor for improved selectivity.

## FUTURISTIC PULPING

Will the kraft pulping process fall from its position of overwhelming dominance? The audience received help answering this question through presentations on

several potential rivals, differing in how far they are along the road to commercialization. These range from the commercially untried biopulping to an alcohol pulping process that has been convincingly demonstrated in a semicommercial pilot plant. All offer at least a possibility of producing pulps that can be bleached to high brightness with little or no chlorine.

Wallenberg laureate T. Kent Kirk of the U.S. Department of Agriculture Forest Products Laboratory summarized progress to date in his group's development of biopulping. This is similar to chemimechanical pulping, except that chemical treatment of the chips prior to refining is replaced by treatment, for a period of weeks, with fungi and nutrients. When aspen is the raw material, the product has properties similar to those of CMP. Lower energy requirements and reduced potential for environmental effects offer tradeoffs for the long treatment time.

Solvent pulping was the subject of two presentations reflecting North American and European experience, respectively. In the former case, the speaker was Herbert L. Hergert of Repap Technologies. He classified existing processes according to the chemical nature of the solvent systems they employ and also according to their progress toward commercialization. Only two processes are at the semicommercial stage and none is at the stage of full commercialization. One of the two semicommercial processes, of course, is Repap's ethanol-based Alcell process, operating in a 35-ton/day demonstration plant at Newcastle, New Brunswick. It produces kraft-like pulp from a mixture of birch, maple and aspen. A 300-ton plant is in the engineering phase and is scheduled to go on-stream in 1993.

The European view was provided by R. Patt of the University of Hamburg. He described the status of the four leading contenders, Acetosolv (85% acetic acid), Milox (85% formic acid, 2-6% H<sub>2</sub>O<sub>2</sub>), Organocell (50% methanol first stage, 35% methanol second stage, with alkali and AQ addition to the second stage) and ASAM (alkaline sulfite-AQ-methanol). In Patt's opinion, the last is the most promising, giving kraft-like pulps that are bleachable in nonchlorine sequences.

## OXYGEN AND OZONE

Oxygen use in the bleach plant was the subject of three presentations. Gratzl covered the general principles of delignification and bleaching with oxygen (as well as with hydrogen peroxide and ozone), Olof Samuelson of Chalmers University of Technology in Sweden reviewed recent results obtained in the development of his Prenox process, and Hou-Min Chang of N.C. State treated the technology of oxygen delignification and oxidative extraction.

Discussions of ozone bleaching were provided for three classes of processes, differing with respect to the range of consistencies at which ozone is applied. Technologies based on high, medium and low consistency were reviewed, respectively, by Norman Liebergott of Paprican, Herbert Sixta of Lenzing AG in Austria, and Dr. K. Schwarzl of Voest-Alpine, Linz, Austria.

Liebergott, a proponent of ozone bleaching, presented a wealth of data on ozone properties, as well as on its behavior as a delignifying agent. Among the points he made were that an alkaline extraction stage is needed after the ozone stage; that peroxide can be beneficially added to the ozone stage; and that, at a given level of pulp strength, ozone bleached pulps have lower viscosity than conventionally bleached pulps.

Sixta's presentation was an account of Lenzing's development of the medium-consistency ozone stage to replace hypochlorite in an (EOP) HP sequence. Laboratory development was successful and was followed by successful operation of a 120-metric-ton/day pilot/production unit. Ozone is applied in a fluidizing mixer to achieve a controlled gas-to-liquid ratio. Aspiring ozone bleachers of kraft pulp should note that the Lenzing operation produces hardwood magnesium bisulfite dissolving pulp, and that the kappa number reduction achieved in the MC ozone stage is only about one unit.

Low-consistency ozone delignification is claimed to be more selective than the high-consistency alternative. It has, however, shared a particular difficulty with its medium- and high-consistency counterparts: the necessity to utilize the large excess of oxygen in the mixture of oxygen and ozone issuing from the onsite ozone generator. Since the generator feed must be both dry and uncontaminated by reaction byproducts, this requires making provisions for cleaning and drying the gas stream coming from the bleaching reactor before recycling it to the generator. A solution may be at hand in the form of the Voest-Alpine low-consistency ozone bleaching process described by Dr. Schwarzl. Instead of the oxygen-ozone stream being routed from the generator directly to the bleaching reactor, it is diverted to a pressurized absorption column where the ozone is dissolved in water. The resulting aqueous ozone solution then goes to the bleaching reactor, and the stripped oxygen stream from the absorption column only has to be dried before being recycled to the generator. The concentration of the ozone solution is maintained at a high value by operating the column at pressures up to 10 atmospheres and recycling part of the absorbed ozone back to the column by way of a flash column.

## HYDROGEN PEROXIDE, ETC.

Dominique Lachenal of Ecole Francaise de Papeterie presented his assessment of hydrogen peroxide in its separate roles as a delignifying agent and as a bleaching agent. He was not optimistic about its future as a delignifier, although it can remove 40% of the lignin in kraft pulp. His pessimism is based on the fact that peroxide is less selective than oxygen, which he believes is due to potentially harmful radicals being formed mainly in the vicinity of the lignin component in oxygen bleaching; whereas, in peroxide delignification these radicals are formed everywhere in the pulp suspension as a product of peroxide decomposition. Peroxide brightening, on the other hand, is effective by virtue of its ability to convert carbonyl groups (such as those introduced by a preceding oxygen stage) into carboxyl groups that impart less color and greater solubility to lignin residues.

The use of less conventional peroxide systems was described by Ray Francis of the Empire State Paper Research Institute. These systems are generally more electrophilic than hydrogen peroxide and are used under acidic conditions. They include peracetic acid, performic acid, monopersulfuric acid and peroxidic species formed upon addition to hydrogen peroxide of oxyanions such as molybdate. Results achievable with such systems were exemplified by data previously presented by Howard Rapson, showing that kraft pulp can be bleached to 86 brightness and 16 cp. TAPPI viscosity using only peracetic acid and alkali.

In a sharp departure from all the talk about peroxides, Norm Liebergott described what can be achieved with reducing agents. Apart from the well-known effects of hydrosulphite on mechanical pulps, these achievements are few. Sodium borohydride in a second caustic extraction stage can improve brightness while decreasing reversion and yellowness. In addition, hydrosulfite shows promise as a "color stripper" in the bleaching of recycled pulps.

The last two formal presentations rounded out the biotechnology group begun earlier by Kent Kirk's talk on biopulping. M.G. Paice of Paprican discussed the intriguing topic of enzymatic bleaching and Tom Joyce explored known and potential interactions of the bleaching process with biological effluent treatment systems. Results reviewed by Paice showed that xylanase pretreatment can result in savings of 10-35% chlorine, depending on wood species, with corresponding AOX reductions. The enzyme pretreatment can also considerably enhance delignification in subsequent oxygen and peroxide stages.

## PUTTING IT ALL TOGETHER

Douglas Reeve of the University of Toronto led the first of two panel discussions titled "Putting it All Together—Sequences of the Future." His theme was that chlorine dioxide has a bright future. He contends that, even in the most stringent environmental scenario, chlorine dioxide is worth saving because it is efficient and economical and produces pulp of high strength, cleanliness, brightness, and stability. A cogent observation by Reeve: "Economics will play a strong countervailing role to environmental demands."

Peder Kleppe, of M. Peterson and Son A.S., followed with his pulping and bleaching proposal for the future. It is built around polysulfide-AQ pulping to kappa 60, two-stage oxygen delignification to kappa 20, ozone activation, pressurized (EOP) treatment, another ozone stage, and a final peroxide stage. In addition to the obvious lack of reliance on chlorine-containing compounds, the following advantages are claimed for this sequence: high yield, high pulping capacity, low refining energy, and the possibility of mill water system closure.

A reactivity-based classification of bleaching agents was offered by Dominique Lachenal. He observed a kinship between chlorine and ozone inasmuch as both possess the ability to react with free and etherified phenolic groups. Similarly,



oxygen and chlorine dioxide, both radicals, react principally with free phenolic groups and may be categorized together. Finally, hydrogen peroxide and hypochlorite react almost exclusively with carbonyl groups. Since each of the three groups has a chlorine-free member, Lachenal is optimistic about the prospects for nonchlorine bleaching.

The last of the first set of panelists was Rudra Singh, of N.C. State. He outlined what he saw as the many advantages of ozone bleaching and intimated that two new North American ozone bleaching installations would be announced during the third quarter of 1991.

The second set of panelists addressed their remarks to the theme "Future Directions and R&D Needs." Tom McDonough led by enumerating three research needs: understanding kinetics to achieve selectivity, seeking novel bleaching methods, and defending chlorine. Selectivity is a manifestation of differences between the respective rate laws for delignification and polysaccharide degradation; determining them would provide a complete description of the important process variable effects. The search for novel bleaching methods would benefit from a better appreciation of the relationship between residual lignin structure and reactivity/selectivity of its reactions with nonchlorine bleaching agents. Finally, it is important to gain a better understanding of the nature of the chlorinated organic materials formed during bleaching and how it depends on the process.

Nils Hartler envisioned extended MCC, perhaps to kappa numbers as low as 15, followed by oxygen delignification, perhaps with a selectivity-enhancing pretreatment in between. He also saw a place for ozone, but with a limited mission, perhaps 15% delignification. Leaching of high-molecular-weight lignin from the fiber in a slow diffusion process is another bet we shouldn't miss. The low-lignin content pulp resulting from these steps will, in Hartler's view, be subjected to final bleaching with chlorine dioxide and alkali.

Herb Hergert, the third panelist, advised talking to people in printing plants before finalizing research plans. He also placed high priority on solving the CTMP reversion problem, learning more about the recycling of coated and wood-free grades (and developing new printing and ink technology to facilitate it), and developing fast-growth temperate forests to meet the eucalyptus threat.

The final panelist, Jean Renard of International Paper, emphasized the importance of assessing the long-term environmental impact of effluents being produced by today's pulping and bleaching processes, doing research aimed at better processes, and revisiting the closed-cycle mill concept.

In the discussions following the various presentations, vigorous exchanges of views occurred. Some disagreement arose on such matters as whether chlorine dioxide would survive the environmentalist onslaught; whether reductive bleaching agents have a future; whether toxicology and epidemiology would prevail over politics, perceptions and suspicions; whether economic and legal realities would prevail over environmental demands; whether concepts such as AOX should be dignified

by scientific study; and whether human welfare is better served by a healthy industry or by air and water emissions that are so scrupulously clean as to be beyond suspicion. Nonetheless, the information transfer that occurred here can only serve to bring the industry and the community closer to a mutually agreed upon new order.